DEVELOPMENT OF HIGH THERMAL BUILDING NANO-INSULATION MATERIAL USING PU NANOCOMPOSITES FOR ROOFING APPLICATION

INTAN YUSNIZA MOHAMAD

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UNIVERSITI MALAYSIA PAHANG

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ABSTRACT

Polyurethanes (PUs) are one of the most versatile classes of materials today and their demand as a high thermal insulator material continues to grow. The widespread application of PUs necessitates understanding the chemistry elements that improve the thermal stability and mechanical strength as these are crucial prerequisites to obtain the high performance of thermal insulator material for the structures and buildings. The first part of the experiment focuses on the modification of pristine clay with Transition Metal Ions (TMIs), Copper and Ferum using methanol solvent. The objectives of surface modification of pristine clay is due to the incompatibility between hydrophilic clay and hydrophobic polymer. After these modifications, the samples of organoclay are characterized using some sophisticated methods like Fourier Transform Infrared (FTIR) and Field Emission Scanning Electron Microscopy (FESEM). FTIR and FESEM results illustrated modified nanoclays had smoother surfaces of pristine clay or montmorillonite (MMT) which proved that modification has taken place successfully. The samples then tested by Thermal Gravimetry Analysis (TGA) and Tensile Test to measure their thermal and mechanical properties respectively. Both the thermal stability and mechanical strength showed positive improvements. Thermal stability is hypothesized to have increased significantly, due to the transition metal ions hindering the pristine clay within the polymer matrices from decomposing easily. The stronger interfacial interaction causes to the increasing of stress at break and the weak interfacial forces may lead to some decreasing of stress at break for nanocomposite. Further research will be required to commercialize findings.

Keywords : Modification, Nanoclay, Montmorillonite, Organoclay, Transition Metal Ions (TMIs), Solution Intercalation, Thermoplastic Polyurethane (TPU), Thermal Stability, Mechanical.

ABSTRAK

Polyurethanes (PUs) adalah salah satu kelas yang paling serba boleh hari ini dan permintaan mereka sebagai bahan penebat haba yang tinggi terus berkembang. Permohonan meluas memerlukan unsur-unsur kimia yang meningkatkan kestabilan haba dan kekuatan mekanikal kerana ini adalah prasyarat penting untuk mendapatkan prestasi yang tinggi bahan penebat haba bagi struktur dan bangunan. Bahagian pertama eksperimen memberi tumpuan kepada pengubahsuaian dari tanah yang asli dengan Peralihan Logam Ion (TMIs), tembaga dan ferum menggunakan pelarut metanol. Objektif pengubahsuaian permukaan tanah liat yang bersih adalah disebabkan oleh ketidakserasian antara tanah liat hidrofilik dan polimer hidrofobik. Selepas pengubahsuaian ini, sampel organo dicirikan menggunakan beberapa kaedah yang canggih seperti Fourier (FTIR) dan Pelepasan Imbasan Elektron Mikroskop (FESEM). Nanoclays diubahsuai dan keputusan FTIR dan FESEM digambarkan mempunyai permukaan licin bagi tanah liat yang asli atau montmorilonit (MMT) yang membuktikan bahawa pengubahsuaian telah berlaku dengan jayanya. Sampel kemudiannya diuji oleh Analisis terma gravimetri (TGA) dan Tegangan Ujian untuk mengukur sifat haba dan mekanikal mereka masing-masing. Kedua-dua kestabilan haba dan kekuatan mekanikal menunjukkan peningkatan positif. Kestabilan terma hipotesis telah meningkat dengan ketara, disebabkan oleh ion logam peralihan menghalang tanah liat yang bersih di dalam matriks polimer daripada penguraian mudah. Interaksi antara muka yang lebih kukuh menyebabkan peningkatan tekanan dan kuasa-kuasa antara muka yang lemah boleh membawa kepada beberapa penurunan tekanan untuk nanocomposit. Penyelidikan selanjutnya diperlukan untuk mengkomersilkan penemuan.

Kata Kunci: Pengubahsuaian, Nanoclay, montmorilonit, organo, Peralihan Logam Ions (TMIs), Penyelesaian Interkalasi, Termoplastik Poliuretana (TPU), Kestabilan terma, Mekanikal.

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LIST OF ABBREVIATIONS

AAS	Atomic Adsorption Spectrometer
ABS	Acrylonitrile-butadiene-styrene
EDTA	Ethylenediaminetetraacetic acid
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform InfraRed
ICPMS	Inductively Coupled Plasma Mass Spectrometry
IPDI	Isophoron diisocyanate
MDI	Diisocyanates 4,4'-methylene bis(phenyl isocyanate)
MMT	Montmorillonite
PNS	Polyurethane Nanocomposites
PTMEG	Polytetramethylene glycol
PU	Polyurethane
TDI	2,4-toluene diisocyanate
TEM	Transmission Electron Microscopy
TGA	Thermal Gravimetric Analysis
TMI	Transition Metal Ions
TPU	Thermoplastic Polyurethane
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Motivation and Statement of Problem

An ever increasing demand for energy saving in various areas coming to realize that there is a crucial need to reduce energy usage in buildings and it has to be done in an effective way. As buildings constitute a substantial part of the total energy consumption, savings within the building sector will be important, both for existing and new buildings. One of the key fields will be thermal building insulation materials and solutions. Recent studies (McKinsey, 2009) show that energy efficiency measures are the most cost-effective ones. As a result of increased energy cost and environmental concerns, insulation has become a priority in homes or public buildings to make important savings.

The traditional thermal building insulation materials have the drawback that they require rather thick building envelopes in order to meet the increasingly demanding thermal insulation requirements. Increasing the building envelope thickness up to between 400 and 500 mm, e.g., by use of mineral wool and similar insulation materials, forces new challenges both with respect to building physics and practice. In addition, such thick envelope structures are less cost-effective at locations where the area is restricted, i.e. by restrictions in physical dimensions or by high living area costs per square meter (Rehab & Salahuddin, 2005). Thus, with increasing thermal insulation, there is a strive to not increase the thickness of the building envelope substantially. For good work and comfortable life, human need buildings with a good indoor climate,

which does not depend on weather conditions during the year. Thus, there should also be an aim to invent or develop new robust high performance thermal building insulation materials without the disadvantages.

Nowadays, type of insulating materials in use includes expanded and extruded polystyrene foams, rigid polyurethane foam, glass wool, or cellulosic fiber. However, their combination of performances and relatively low cost, polyurethane nanocomposites is ranked amongst the most popular choices for insulation. A polymer composite is made by the combination of a polymer and synthetic or natural inorganic filler. Fillers are incorporating to improve the desired properties of the polymer or simply reduce the cost. Nowadays, polymer composites have turned to a state of the art as engineering materials. Polymer composites with improved mechanical, thermal, and barrier properties are widely used in many applications. Even so, by the application of conventional fillers such as talc, fibers, calcium carbonate etc, it often requires to use a large amount of filler in the polymer matrix to have a good improvements in the composite properties which may result in some other undesired properties such as brittleness or loss of opacity (Zhang & Friedrich, 2003).

1.2 Objectives

The following are the objectives of this research:

I. To modify the surface of nanoclay to improve the interaction with thermoplastic polyurethane.
II. To fabricate polyurethane-modified clay nanocomposite.
III. To study the mechanical and thermal properties of polyurethane nanocomposite.

1.3 Scope of This Research

In order to achieve the objectives, the following scope of work are designated :

I. To modify clay using Catalytically Activated Metal Ion (TMI) and characterize using ICPMS and AAS.
II. To fabricate polyurethane-organoclay using solution mixing method.
III. To conduct mechanical and thermal test using Thermal Gravimetric Analysis (TGA) and Tensile Test.

1.4 Main Contribution of This Work

The main contribution of this research is roofing application. The properties of insulation materials depend on their structure, the raw materials used and the manufacturing process. In order to select a suitable thermal insulation material, thermal properties is the prime importance. High thermal stability and tensile strength is the main goal in order to achieve a great performance of high thermal building nano insulation materials for roofing application.

1.5 Organisation of This Thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 is literature review. In this section, it provides a description of the type of polymer chosen, type of nanofiller and also its structure. The other element is the method of preparation polymer nanocomposites, structural characterization and also testing of polymer nanocomposites as well as its properties.

Chapter 3 stated the methodology for modification of clay using an ion exchange method and also the fabrication of PU-Nanocomposites using solution mixing method. This chapter also discusses the methodology for characterization of organoclay and polymer nanocomposites by using AAS, ICPMS, FTIR and FESEM and then the sample were tested by using TGA and Tensile Test for thermal and mechanical properties respectively.

Chapter 4 mainly discusses about the result that collect from the characterization analysis of organoclay and testing of polymer nanocomposites. A detailed description of the analysis and previous research are also presented.

Chapter 5 is conclusion of the entire objectives in this research either it has been taken place successfully.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

This paper presents the description of polymer nanocomposite (PNC) which have received much attention from the scientific research field in the past several years due to their improved properties at very low clay loading levels compared with conventional filler composites (Berta et al., 2006). Polymer nanocomposites has shown vast enhancement in modulus, toughness, and barrier properties as well as mechanical and thermal properties (Xiong et al., 2004). Interests in these materials stem from the fact that there is a unique physical state in the polymer of its silicate-polymer interface. Organoclays are one of the fillers that are commonly used in the polymer industry as a filler. Clay minerals such as montmorillonite (MMT) are ideal reinforcing fillers as it exhibits many interesting structural features such as exchangeable interlayer cations, hydroxyl groups on the edges of clay platelets and a high aspect ratio of the individual layers (Lagaly, 1999). However, as mentioned by Lucilene, (2008), it is important for proper organophilization to occur as it is the key step for successful exfoliation between the clay particles and the polymer matrix. With this exfoliation, a strong interfacial interaction between the polymer matrix and organoclays can be built whereby this interactions aids in improving the properties of the polymer matrix. Polyurethanes have widespread applications as coatings, adhesives, rubbers, foams and thermoplastic elastomers (Asim et al. 2005). Polyurethane can be designed as various applications as it has a wide range of physical and chemical properties. In recent years, polymer

nanocomposites have attracted great interest among researchers because as it exhibits improved performance properties compared to pristine polymers because of their unique phase morphology by layer intercalation maximizes interfacial contact between the organoclay and its matrix (Byung et al., 2002). This chapter is focused on the review of the physical and thermal properties of polyurethane as well as the preparation and properties of polyurethane nanocomposites by using organoclay as the filler.

2.2 Polyurethane

Polyurethane was first developed in the year 1937 by Otto Bayer. It was developed by the polyisocyanate-polyaddition process. Polyurethane then started to become a material to be studied due to its unique properties. The properties of polyurethane can be adjusted via two approaches whereby the first is by changing the molecule structure if polyurethane by modification of its three basic building blocks and the second is by introducing inorganic fillers into the polyurethane matrix (Song et al., 2005). The structure of polyurethane is shown as below.

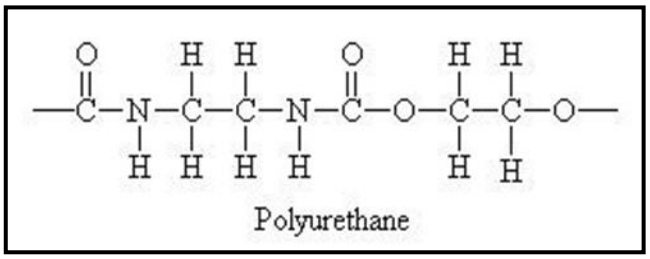

Figure 2.1: Structure of Polyurethane

Source: Otto Bayer (1937)

Polyurethanes find plenty of applications in a wide range of engineering works including in the biomedical field. Polyurethane is belongs to a class of polymer containing organic segments joined to each other by urethane linkages. Otto Bayer and coworkers have invented this polymer at the I.G. Farbenindustrie, Germany in 1937, however production in the industrial scale started only in 1940 when DuPont and ICI recognized its extraordinary elastic properties. The key components required for the synthesis of polyurethanes are:

a. Diisocyanate (aliphatic or aromatic)

b. Polyol (polyester or polyether)

c. Chain extender (low molecular weight diol or diamine).

The most commonly used diisocyanates are 4,4'-methylene bis(phenyl isocyanate) (MDI), 2,4-toluene diisocyanate (TDI), 1,6-hexamethylene diisocyanate(HDI), isophoron diisocyanate (IPDI), etc. Although isocyanates play a vital role in the polyurethane synthesis (due to the differences in their reactivity depending on the presence of aromatic and aliphatic moieties) but the final property of the polyurethane are mostly determined by the type of polyol used. Function of the polyols may vary from 2 to 8 with an average molecular weight of 400 to 6000 grams per GM mole (Mn). In practice, polyol with molecular weight 1000 and 2000 grams per GM mole are most widely used (Pandey et al., 2005). Polyether polyol based polyurethanes are more resistant to hydrolysis, whereas, the polyester polyol based counterparts are thermally more stable. Polytetramethylene glycol (PTMEG) based polyurethane possess excellent hydrolytic stability and microbial resistance, outstanding dynamic properties including resilience and low temperature flexibility. The third most important component is the chain extender. The most widely used chain extender in preparing polyurethanes is 1,4-butane diol but methylene bis (O-chloro aniline) is normally used for the preparation of polyurethane urea (Hussain et al., 2006).

Catalysts play an important role in the synthesis of polyurethanes. Tertiary amines are mostly used in the synthesis of polyurethane foams (as it also promotes the reaction of the isocyanate with water). However, organometallic compounds especially dibutyl tin dilaurate is most widely used catalyst for the synthesis of thermoplastic polyurethanes (TPUs) (Giannelis, 1996).

In the synthesis of polyurethanes, chemistry of diisocyanate plays a important role. The isocyanate group contains a highly electrophilic carbon atom, which possess the resonating structures as shown in Figure 2.2.

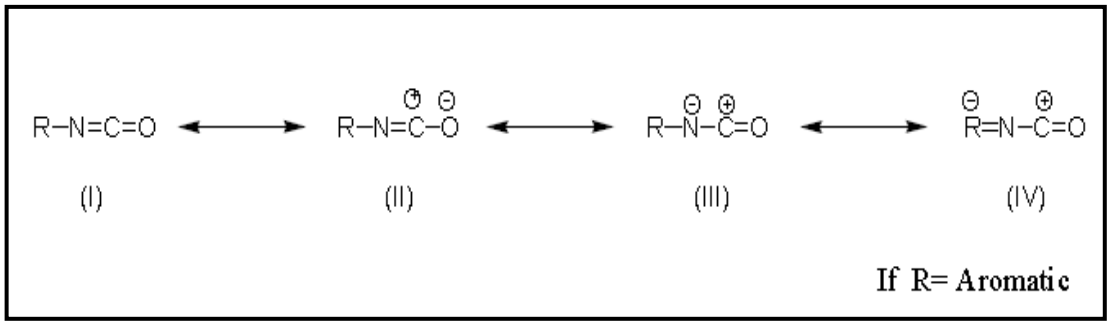

Figure 2.2: Resonating structures of isocyanate

Source: Giannelis (1996)

This electrophilic carbon present in the –NCO group plays a pivotal role in polyurethane chemistry. Three resonating structures (II, III and IV), out of the four, contain carbon atom having positive charge on it with the delocalization of negative charge on oxygen, nitrogen and R group (provided 'R' is aromatic). This is the only reason for the high reactivity of isocyanates towards nucleophiles and higher reactivity of aromatic isocyanates over aliphatic isocyanates. It is also found that the reactivity of aromatic isocyanate containing electron withdrawing group on the aromatic ring increases when present in another- and para- positions. Similarly, the reactivity diminishes significantly when the aromatic ring(s) contains electron donating substituents (Gilman, 1999).

2.2.1 Synthesis of Polyurethane

The methods of synthesis of polyurethanes can be differentiated according to the medium of preparation (bulk, solution, aqueous) and the addition sequence of the reactants (one shot process, two step pre-polymer process). Bulk polymerization (either one shot or two step prepolymer process) is generally preferred in industries as the process is cost effective and environmentally friendly because of solvent-free synthesis, whereas, solution polymerization is being used for laboratory synthesis (Fornes & Paul, 2003).However, reaction in aqueous media via the miniemulsion polymerization technique is mostly limited to the preparation of certain coatings and adhesives (Finnigan et ., 2004).

In one shot process, all the ingredients (polyol, diisocyanate, chain extender and catalyst) are mixed together. Even so, in the prepolymer process, polyol is first reacted with the diisocyanate to prepare the prepolymer, followed by chain extension reaction. In case of one shot process, high degree of shear is required to render homogeneous mixing (Cosoli,2008). Prepolymer process is the most widely used method as one can precisely control the morphology of the final product by this method. Figure 2.3 depicts the schematic representation of synthesis of polyurethanes by the propeller route.

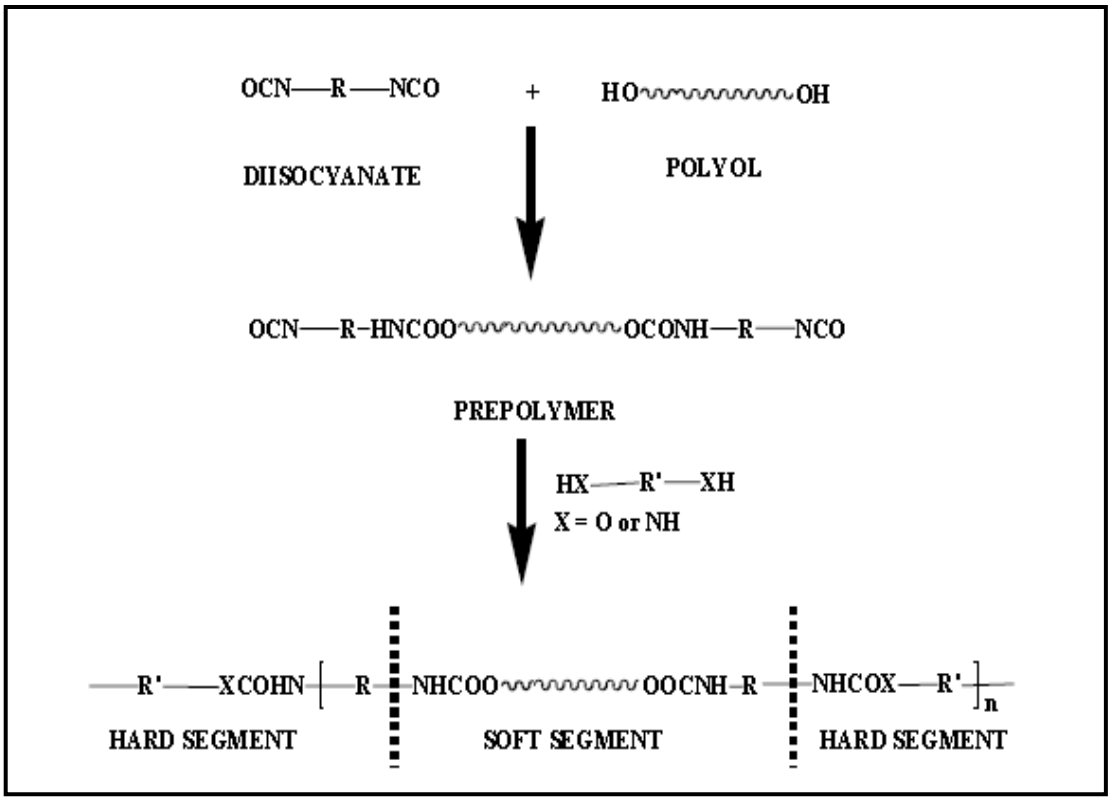

Figure 2.3: Preparation of polyurethane by prepolymer method

Source: Fornes & Paul (2003)

Polyurethanes can be classified into various categories depending on their properties and applications. Thermoplastic Polyurethane (Segmented polyurethane) – ranging from thermoplastic to thermoplastic elastomer

b. Castable Polyurethane

c. Millable Polyurethane

d. Polyurethane foams (Rigid and Soft)

e. Coatings

f. Adhesives.

2.2.2 Thermoplastic Polyurethane

Amongst all the grades of polyurethanes, TPU is the most widely used material. This is because of its higher mechanical strength, excellent abrasion resistance, ease in processing and bio-compatibility. TPU is a block copolymer composed of hard segments and soft segments arranged in a (A-B-A). The soft segment is prepared by the reaction between the poll and the discount, but hard segment is formed by the reaction between the discount and the chain extender. Phase separation (segregation) between the hard and soft segments occurs due to the difference in secondary forces (van der Waals, dipole-dipole, H-bonding interactions, etc.(Chingwada & Wildie, 2003). Thus, the degree of segregation between the hard and soft segments depend on the extent of interaction of the hard segments with each other and also with the soft segments (Krikorian & Pochan, 2003).

The phase segregation is less pronounced in polyester polyurethane than in polyester polyurethane and is most pronounced in polybutadiene based (e.g., HTPB) polyurethane. Also a drastic development in phase segregation and domain organization can be encountered due to the incorporation of urea moiety in the hard segment (Meneghetti & Qutubuddin, 2006), which causes improved mechanical strength such as higher mechanical properties, lower hysteresis, greater toughness and slower rate of stress relaxation (Sheng et al., 2004). Phase separation increases with increasing chain length of soft segment or with the increasing polarity leading to lesser hard-soft segment interactions . Bonart et al., (2006)reported the first direct evidence of the occurence of two-phase morphology from small angle X-ray scattering (SAXS) study.

Despite several advantages, TPU suffers from lower thermal stability and flame retardancy as compared to other engineering thermoplastics (polyester amides, polyester esters etc.) for similar applications (Lebaron et al., 1999).

2.2.3 Applications of Polyurethane

Polyurethane is one of the polymers that are highly ranked in the polymer field due to its unique properties that can be altered according to the application that is to be applied. Polyurethanes can be tailored to meet the highly diversified demands of modern technologies such as coatings, adhesives, fiber, foam and thermoplastic elastomers (Beyer, 2002).

According to Subrata et al. (2012) segmented polyurethanes are extensively used polymers in biomedical applications because of their bio-stability, biodegradability and tailorable backbone structure from a wide range of available precursors. Furthermore, their unique combination of biocompatibility, toughness and functionality has led to the widespread use in implantable devices such as vascular grafts, pacemaker leads, blood bags, bladders and artificial hearts that depend on elastomeric properties for interaction with, and mimicking of, soft tissue (Thostenson, 2005).

PU is also used widely in the coating area. According to Chigwada et al. (2006), the wide applicability of PU coatings is due to versatility in selection of monomeric materials from a huge list of macrodiols, discounts and chain extender (CE). PU coating are found on many materials such as on automobiles to improve the colour retention, in construction and as spray coating for durability against environmental deterioration.

With the increasing demand of polyurethane's usage, the development of polyurethane nanocomposites can be an added value for improvising and utilizing the full benefits of this polymer in its applications.

2.3 Nanofillers

2.3.1 Layered Silicate

The layered silicates are natural or synthetic minerals consisted of the regular stacks of aluminosilicate layers with a high aspect ratio and high surface area. Layered silicates are easily available and have low cost. The current most common layered silicates used in polymer nanocomposites preparation are clays. Clay is referred to a part

of soil fraction with the particle size of less than 2 μm. The clay layers have a thickness of about 1 nm which is at the nanoscale. There are many members of clays with some difference in their formula, properties and structure including swelling and exfoliation (Yano et al., 1993). Those members who are able to be exfoliated by polymer chains or monomers and distributed as individual clay layers within a polymer matrix are suitable for the preparation of polymer nanocomposites. The individual clay layers can lead to the dramatic improvements in polymer properties due to their high aspect ratio and high interfacial interactions with polymer matrix (Zanetti et al., 2004).

2.3.2 Structure of Clays

Clays have layered structure. The layers are built from tetrahedral sheets in which a silicon atom is surrounded by four oxygen atoms and octahedral sheets in which a metal like aluminium or magnesium is surrounded by eight oxygen atoms. The tetrahedral (T) and octahedral (O) sheets are fused together by sharing the oxygen atoms. Unshared oxygen atoms are exhibit in hydroxyl form. Two main arrangements of octahedral and tetrahedral sheets bind together make the one layer structure of clay. One tetrahedral bound to one octahedral (1:1) is known as kaolin group with the general composition of $Al_2Si_2O_5(OH)_5$ and the layer thickness of ~ 0.7 nm. The crystal lattice consisted of one octahedral sheet sandwiched between two tetrahedral sheets (2:1) with the total thickness of 0.94 nm is well known as phyllosilicates. The 2:1 phyllosilicate layers might be electrostatically neutral with no inter layer ion present known as pyrophyllite. As no presence of inter layer ions, the layers do not expand in water. When silicon in tetrahedral sheets is altered by aluminium, the 2:1 structure is known as mica (Yao et al., 2004).

The negative charge generated by this substitution is balanced by the insertion of potassium cations between layers. Due to the equal size of potassium cation and the hole created by Si/Al tetrahedral sheets, the presence of potassium cation makes no inter layer spacing. Therefore, the 2:1 layers are held together strongly and the swelling or

exfoliation of layers is not possible. When in neutral pyrophyllite, the aluminum cations in the octahedral layers are partially substituted by divalent magnesium or iron cations the smectite clay group is formed. The negative charge generated by this substitution is balanced by inter layer counter sodium or calcium ions. The charge created on the layers is not locally constant and varies from layer to layer (Yeh et al., 2008). An average charge value is evaluated for the layers which can be determined by cation exchange capacity (CEC) measurement. Due to the unequal size of inter layer cations with the holes of tetrahedral sheets, the presence of inter layer cations causes to an interlayer spacing. The layers stay near together with a regular gap between them. The gap is known as inter layer or gallery. The thickness of the repeated units in a regular multilayer structure contained of one layer and one inter layer space is called d-spacing (d001) or basal spacing . The basal spacing of clays can be measured or calculated from their X-ray diffraction patterns. The inter layer dimension is also depending on the clay nature and swelling or hydration degree of inter layer cations. The inter layer distance is around 1 nm for montmorillonite (Kornmann et al., 2003).

The van der waals and electrostatic forces stacked the layers together are relatively weak and inter layer distance varies depending on the charge density on the layers, its degree of hydration and inter layer cation radius. Because of the inter layer spacing and weak inter layer forces, the cations present between the layer might be hydrated in aqueous solutions known as clay swelling. The swelling cause increasing of inter layer space. The charge of density on the clay layers is differ in various clay groups with different clay structures (Mittal, 2007). Due to the inter layer spacing and weak forces between layers, especially in the hydrated form, other molecules also can be intercalated between layers, leads to the expanding of layered lattice and finally may be caused by the separation of individual layers. The unique exfoliation/intercalation behavior of smectite clay minerals which is responsible to the high aspect ratio of this clay type makes them very important and powerful as reinforcing filler for polymers.